

Bel. to corresp. to N° 25,55.805

⑪ (A) No. 1064957

④⑤ ISSUED 791023

⑤② CLASS 260-466.8
C.R. CL.

⑤① INT. CL. ² C07C 69/96

①⑨ (CA) **CANADIAN PATENT** ①②

⑤④ PROCESS FOR THE PREPARATION OF POLYCARBONATES

⑦⑦ Senet, Jean-Pierre; Cau, Alain A.,
France

Granted to Société Nationale des Poudres et
Explosifs, France

②① APPLICATION No. 240, 852

②② FILED 751201

③⑦ PRIORITY DATE France (74 40838) 741211

No. OF CLAIMS 4 - No drawing

ABSTRACT OF THE DISCLOSURE

Linear aliphatic polycarbonates having terminal hydroxyl groups are produced by transesterification between a diol and diethyl carbonate, the transesterification being carried out in two stages:

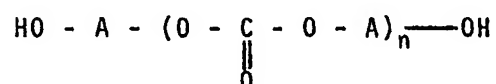
(a) in the first stage, the reaction is carried out in the presence of a basic catalyst at a temperature below 150°C, and

(b) in the second stage, the reaction is completed in a thin film evaporator, the heating medium supplied to the evaporator being at a temperature above 160°C.

The products obtained by this process are useful for the production of polyurethane elastomers which are resistant to hydrolysis.

The present invention relates to a process for the preparation of linear aliphatic polycarbonates which have terminal hydroxyl groups and a number average molecular weight of from 500 to 3000, and the number of functional groups of which is greater than 1.95.

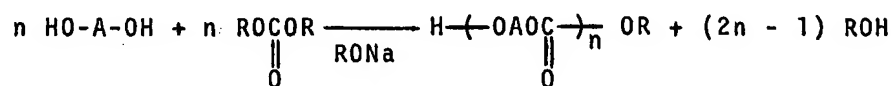
These oligomers, which will hereinafter be referred to as "aliphatic polycarbonate-diols" have the following formula:



- 10 in which A is a difunctional linear aliphatic or cycloaliphatic radical containing more than 4 carbon atoms.

PRIOR ART

The preparation of aliphatic polycarbonates by transesterification between a diol and a dialkyl carbonate is described in the works of CAROTHERS, VAN NATTA and HILL (J. Am. Chem. Soc., 52, 314, 1930 and 55, 5031, 1933).



- 20 The reaction is carried out at an elevated temperature (120 to 220°C) in the presence of strongly basic catalysts, such as alkali metal alcoholates. This type of process is described, in particular, in U.S. Patent 2,787,632.

As H. SCHNELL indicates in "Chemistry and Physics of Polycarbonates" (Wiley & Sons, 1964, page 15), it is impossible to obtain polymers of high molecular weight by means of this process, since the presence of a basic catalyst leads, at the temperatures employed, to degradation of the polycarbonate. Likewise, this process does not enable aliphatic carboxylate-diols having a sufficient number of functional groups, that is at least 1.95, to be prepared.



If, in the preparation of aliphatic polycarbonate-diols, an attempt is made to avoid the degradation reactions by carrying out the transesterification at a lower temperature (below 150°C), the removal of the alcohol formed is incomplete and the product obtained contains a significant proportion of unreactive terminal groups of the formula ROCOA- .

U.S. Patent 2,210,817 described a technique which enables aliphatic polycarbonates of high molecular weights to be obtained. This technique consists of destroying the basic catalyst (when most of the alcohol has been removed by heating at 200°C under reduced pressure) and of terminating the reaction under a high vacuum in the presence of traces of a carboxylic acid salt.

This procedure cannot be applied directly to the synthesis of aliphatic polycarbonate-diols by transesterification between a diol and diethyl carbonate, principally for the following reasons:

- (a) The reaction mixture always has a high content of hydroxyl groups, even at the end of transesterification. Since these groups, in the presence of bases, catalyse degradation reactions, the temperature must not exceed 140°C (instead of 200°C); it is thus difficult, if not impossible, to achieve a degree of forward reaction higher than 99%, and
- (b) The second step is difficult to carry out because of the problem of regulating the molecular weight of the final product.

THE INVENTION

We have now found that it is possible to prepare aliphatic polycarbonate-diols having a satisfactory number of functional groups by transesterification between a diol and diethyl carbonate. According to the present invention, this

process comprises two stages,

in the first stage, the transesterification is carried out in the presence of a basic catalyst at a temperature below about 150°C , and

in the second stage, the transesterification is completed in a thin film evaporator, the heating medium supplied to the evaporator being at a temperature above about 160°C .

The first stage of the process is suitably carried out in a conventional reactor equipped with a stirrer and an effective distillation column which enables the ethanol formed to be separated from the diethyl carbonate. The alcoholate used as catalyst can be prepared by adding sodium to the previously dried diol; from 0.1 to 0.5 g of sodium is preferably used per mol of diol. The temperature is preferably raised gradually from 90° to 140°C and should at no time exceed 150°C . Distillation is stopped when an amount of ethanol corresponding to 70 - 80% of the theoretical amount has been collected.

In the second stage, the reaction mixture resulting from the first stage is introduced into a thin film evaporator. The temperature of the heating medium in the double jacket of the evaporator is preferably from 190° to 250°C . The product obtained is treated immediately with an inorganic acid, dissolved in a water-immiscible solvent and washed with pure water.

Aliphatic polycarbonate-diols having strictly two functional groups are of great value for the preparation of polyurethane elastomers which are resistant to hydrolysis.

In order that the invention may be more fully understood, the following example is given by way of illustration only.

1064957

EXAMPLE

The following equipment was used:

a 1 litre glass reactor equipped with an efficient stirrer, a thermometer and a distillation column,

a double jacket distillation column packed with "Fenske" coils (useful length 500 mm, diameter 25 mm) equipped with a reflux head under manual control, and

a stainless steel LEYBOLD thin film evaporator (heating surface area 200 cm^2).

10 358.1 g of hexane-1,6-diol and 60 g of anhydrous benzene were introduced into the reactor which was provided with a short distillation column, in order to remove water initially present in the hexanediol by azeotropic distillation. When all the benzene had been distilled off, the temperature of the reaction medium was reduced to $70 - 80^\circ\text{C}$ and 0.6 g of sodium was added with stirring. After the latter had reacted completely, 304.3 g of diethyl carbonate were introduced. The reactor was equipped with the distillation column as first specified above and the mixture was heated whilst stirring
20 vigorously.

When the temperature of the mass reached $95 - 100^\circ\text{C}$, the ethanol began to distil. Refluxing was regulated so that the temperature at the top of the column was equal to $78.5 \pm 0.5^\circ\text{C}$. The temperature of the reaction medium was raised gradually to 140°C . Distillation was stopped when 197.5 g of ethanol had been collected. This distillation lasted for 30 minutes.

The reaction mixture was cooled rapidly to 60°C and was introduced, at the rate of 0.9 litre/hour, into the thin
30 film evaporator under a pressure of 10 mm Hg. The temperature of the heating fluid supplied the double jacket was 200°C .

1064957

Under these conditions, the time taken for the product to pass through the evaporator was approximately 80 seconds.

The non-volatile product was collected and treated immediately with a slight excess of anhydrous hydrogen chloride, (so as to ensure destruction of the basic catalyst).

The oligocarbonate was dissolved in 300 ml of dichloromethane and the organic phase obtained was washed once with 500 ml of water and dried over anhydrous sodium sulphate. After removing the solvent by evaporation under reduced
10 pressure, the product was stirred vigorously at 140° under 2 - 3 mm Hg for 30 minutes.

The aliphatic polycarbonate-diol obtained was in the form of a white wax which was soluble in the cold in the following solvents: toluene, dichloromethane, acetone and ethyl acetate.

The physico-chemical characteristics were as follows:

hydroxyl content: 0.75 equivalent/kg

(acetylation method)

acidity: 1.5×10^{-3} equivalent/kg.

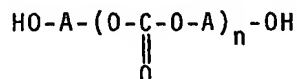
20 This polycarbonate was converted into a polyurethane reaction with diphenylmethane diisocyanate and butane-1,4-diol ("one shot" formulation), the molar ratio $\frac{\text{NCO}}{\text{OH}}$ being equal to 0.95.

A film was produced by compression moulding of the polyurethane obtained; this film had a tensile strength of more than 400 kgf/cm² (NFT Standard Specification 46,002).

1064957

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the preparation of a linear aliphatic polycarbonate-diol corresponding to the formula:



wherein A is a difunctional linear aliphatic or cycloaliphatic radical containing more than 4 carbon atoms, said polycarbonate-diol having an average molecular weight of from 500 to 3000 and the number of functional groups being greater than 1.95, which comprises two stages:

in the first stage, the transesterification is carried out in the presence of a basic catalyst at a temperature below about 150°C, and

in the second stage, the transesterification is completed in a thin film evaporator, the heating medium supplied to the evaporator being at a temperature above about 160°C.

2. A process according to Claim 1, in which the basic catalyst is formed by adding sodium to the reaction mixture.

3. A process according to Claim 2, in which an amount of sodium used is from about 0.1 to about 0.5 g per mol of diol.

4. A process according to Claim 1, in which the heating medium supplied to the evaporator is at a temperature of from about 190°C to about 250°C.

